Room-Temperature Nanoimprint using Sol-Gel ITO Film

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We report room-temperature nanoimprint (RT-NIL) process using sol-gel indium tin oxide (ITO) as a replicated material. The spin-coated ITO film has to be annealed at over 600 °C to obtain a low resistivity. The spin-coated ITO film can be delineated by RT-NIL, but the patterns disappeared after 200 °C annealing process. To overcome the above problem, we examined the O\textsubscript{2} plasma irradiation effect onto a spin-coated ITO film. As a result, we found that the ITO patterns imprinted by RT-NIL were kept at annealing of 600 °C for 1 hour by O\textsubscript{2} plasma irradiation before annealing.

Keywords: Indium Tin Oxide (ITO), sol-gel, room temperature nanoimprint (RT-NIL)

1. Introduction

Currently, Nanoimprint Lithography (NIL)\textsuperscript{1-3} attracts much interest from many industrial fields because of its many capabilities of providing various nanostructures. NIL, in which resist patterns are fabricated by deforming the physical shape of a resist by embossing it with a mold, promises the high-throughput fabrication of nanostructure devices including quantized magnetic disks and polarization plates. The advantage of NIL is that patterns less than 5 nm in size can be realized over a large area at a high throughput and low cost meaning that highly precise pattern transfer can be performed.

Moreover, with the recent achievement of a high imprint resolution below a few nanometers, there is a consensus forming that supports NIL as the prime candidate for the next-generation lithography.

There are many polymers that can be used as replication materials in NIL. In particular, spin-on-glass (SOG), hydrogen silsesquioxane and sol-gel indium tin oxide (ITO) have useful properties that enable nanoimprinting at room-temperature (RT)\textsuperscript{4,6}. This means that NIL using these sol-gel materials as the replication material completely eliminates the resist-thermal cycle and UV exposure, which are both prone to causing reductions in pattern accuracy and throughput.

Indium Tin Oxide (ITO)\textsuperscript{5,9} is taken of characteristic by high conductivity and high light-transmittance. Therefore, ITO film has been widely used transparent electrode for Liquid Crystal, Solar Panel, and Touch Panel etc.

In this paper, we report RT-NIL process using sol-gel ITO (purchased by Kojundo Chemical Lab. Co. Ltd,}
ITO-05C) as a replicated material. The annealing temperature dependence of resistivity for the spin-coated ITO films was measured, which indicates that the spin-coated ITO film has to be annealed at over 600 °C to obtain a low resistivity. The spin-coated ITO film can be delineated by RT-NIL, but the patterns disappeared after 200 °C annealing process. To overcome the above problem, we examined O₂ plasma irradiation effect onto a spin-coated ITO film. As a result, we found that the ITO patterns imprinted by RT-NIL were kept at annealing of 600 °C for 1 hour by O₂ plasma irradiation before annealing.

2. Room-temperature nanoimprint using sol-gel ITO

Figure 1 shows a schematic of RT-NIL process using sol-gel ITO. (1) First, ITO was spin-coated onto a glass substrate. The film thickness was 300 nm. (2) And then ITO-coated substrate was prebaked at 180 °C for 2 min before nanoimprint. (3) Following, RT-NIL was performed by using the SiO₂/Si mold, which is treated by a fluorinated anti-sticking agent (Optool DSX: Demam solvent = 1:1000 by weight, Daikin Industries). The imprinting temperature, pressure and time were RT, 20 MPa, and 60 sec, respectively. Next, (4b) O₂ reactive-ion-etching (RIE) plasma (2 Pa, 100 W, 50 sccm) was irradiated onto the patterned ITO film for 20 sec. (5) Finally, the ITO film was annealed at 600 °C in vacuum.

3. Annealing effect of spin-coated ITO imprinted pattern

First, we observed the imprinted ITO patterns by a scanning-electron microscopy (SEM). Figure 2 (a) shows the line patterns with 300 nm L&S and 200 nm height before the annealing. The patterns were disappeared after 200 °C annealing as shows in Fig 2 (b). However, the line patterns exposed by O₂ plasma were remained after the annealing. Figures 2 (c) and (d) are with O₂ plasma irradiation before and after 600 °C annealing. The top parts of line patterns after the annealing were dented. Because we used a RIE
as nanoimprint apparatus as a plasma irradiation for the surface oxidization, the whole walls of line patterns were not only oxidized by O₂ radicals but also etched away by an ion sputtering, as shown in Fig.3.

Next, we measured the X-ray photoelectron spectroscopy (XPS) spectra of the ITO films with and without O₂ irradiation. O₂ plasma was irradiated onto the ITO film for 8 min. We used the conventional photoelectron spectroscopy apparatus, which was mounted with a hemispherical electron energy analyzer (VSWCL150). The Mg K line (hv = 1253.6 eV), used as X-ray source, was incident at 45° with respect to the surface normal. The total energy resolution was approximately 1.0 eV. The base pressure in the photoelectron analysis chamber was 2 × 10⁻⁸ Pa.

As shown in Figs. 4 (a) and (b), we measured the wide-scan spectra of ITO film to evaluate O₂ plasma irradiation effect before and after the annealing, respectively. Figure 4 (a) shows that the peak of C1s at 285 eV decreased by O₂ plasma irradiate. That result indicates that ITO film surface was oxidized by O₂ plasma irradiation. Figure 4 (b) shows the peak of C1s was little observed after 600 °C annealing for both spectra. The result indicates that the organic solvent evaporated by ITO film annealing.

Fig.3 Schematic of the surface oxidization using O₂ RIE

Fig.4 XPS spectra of ITO films to evaluate O₂ plasma irradiation effect.
(a) the wide scan before the annealing.
(b) the wide scan after 600 °C annealing

4. Conclusion
The spin-coated ITO film can be delineated by RT-NIL, but the patterns disappeared after 200 °C annealing process. We found that the patterns profiles kept by O₂ plasma irradiation before annealing, because ITO surface was oxidized by O₂ plasma irradiation which was confirmed by XPS measurement. But the top middle parts of line patterns after 600 °C annealing were dented because O₂ RIE is anisotropic plasma. To avoid the dent phenomenon, we should use O₂ plasma with isotropic characteristics instead of O₂ RIE plasma.
References